XCVII.—*Arsinic Acids Derived from Guaiacol and Veratrole. Constitution of the Polyarsenides.*

By Robert George Fargher.

The literature of the organic compounds of arsenic contains no account of the arsinic acids derived from guaiacol and veratrole, though the conversion of *p*-hydroxyphenylarsinic acid into a dihydroxy-acid, presumably 3 : 4-dihydroxyphenylarsinic acid, by means of potassium persulphate has been claimed (D.R.-P. 271892). Trial of this reaction showed that the yield was poor and the product a mixture of 3 : 4-dihydroxyphenylarsinic acid with the unchanged acid. These were separable with difficulty, and their identity was most readily established by complete methylation and fractional crystallisation of the product.

3-Amino-4-hydroxyphenylarsinic acid and 3-*amino*-4-*methoxyphenylarsinic acid* presented an alternative source, but the energetic treatment required to effect the decomposition of their diazo-compounds (compare D.R.-P. 95339; *J. Soc. Chem. Ind.*, 1898, **17**, 314; P., 1905, **21**, 206; French Pats., 167211, 228539) resulted in the almost entire destruction of the arsenical complex. The Bucherer reaction (compare *Ber.*, 1917, **50**, 101, where earlier references are given) also proved to be inapplicable.

The reaction devised by Bart (D.R.-P. 250264, 254092, 254345) therefore presented the most satisfactory method of obtaining the required substances. The preparation of the necessary amines was facilitated by the appearance of a communication by Cardwell and

Robinson (T., 1915, **107**, 257) dealing with 4- and 5-nitroguaiacol and 4-nitroveratrole.

These were reduced to the corresponding amines, which were diazotised and combined with sodium arsenite in alkaline solution, giving rise to 3-*hydroxy*-4-*methoxyphenylarsinic acid*, 4-*hydroxy*-3-*methoxyphenylarsinic acid*, and 3 : 4-*dimethoxyphenylarsinic acid* respectively.

All three acids were readily converted into the corresponding nitro-acids, and the reduction of these was investigated.

On complete reduction with sodium hyposulphite, only 5-*nitro*-4-*hydroxy*-3-*methoxyphenylarsinic acid* was found to undergo the normal reduction to the *arsenobenzene*. 5-*Nitro*-3-*hydroxy*-4-*methoxyphenylarsinic acid* yielded a product containing twice as much arsenic as required by the arsenobenzene formula, whilst 5-*nitro*-3 : 4-*dimethoxyphenylarsinic acid* did not give an insoluble reduction product, probably on account of the formation of a sulphamic acid (compare this vol., p. 372). It was therefore first reduced to the corresponding *amino*-acid. Further reduction also proceeded abnormally, sodium hyposulphite yielding a yellow, insoluble product containing arsenic in the proportion of three atoms to two benzene nuclei, and hypophosphorous acid a black, insoluble powder containing 93 per cent. of arsenic and probably consisting mainly of the free metalloid.

Bertheim has shown (*Chem. Zeit.*, 1914, **38**, 756; compare D.R.-P. 251104, 254226) that the reduction of molecular proportions of two arsinic acids leads solely to the unsymmetrical arsenobenzene.* More recently, Karrer (*Ber.*, 1916, **49**, 1648) has questioned the accepted mechanism of the reaction, and suggested that the symmetrical arsenobenzenes are first formed and then undergo "double decomposition." The latter suggestion amplifies rather than corrects the former, and indicates why, in spite of three possible, and indeed probable, primary reactions, the product consists solely of the unsymmetrical substance.

The generalisation was later extended (D.R.-P. 270354) to mixtures of an aromatic arsinic acid and an inorganic compound of arsenic, such as sodium arsenite, the products resembling those already referred to. The absence of full analytical data—included in the cases under discussion—has, however, left their composition in doubt, although Morgan ("Organic Compounds of Arsenic and

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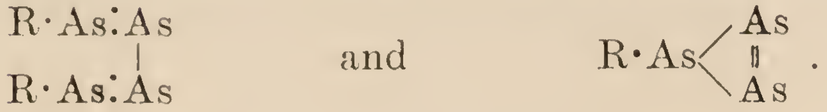
* At the author's request, Mr. W. H. Gray has confirmed Bertheim's statement by reducing molecular proportions of 1 : 3-benzodiazole-5-arsinic acid (T., 1919, **115**, 1372) and 3-amino-4-hydroxyphenylarsinic acid, the properties and composition of the product confirming the unsymmetric formulation.

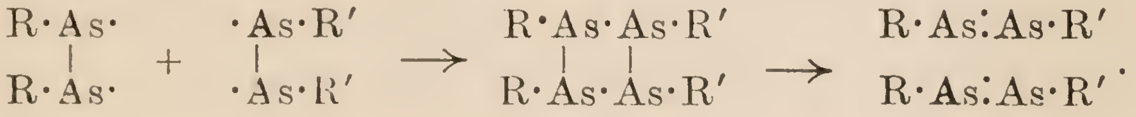
Antimony," p. 270) has suggested that they are possibly compounds of tervalent arsenic corresponding with the general types



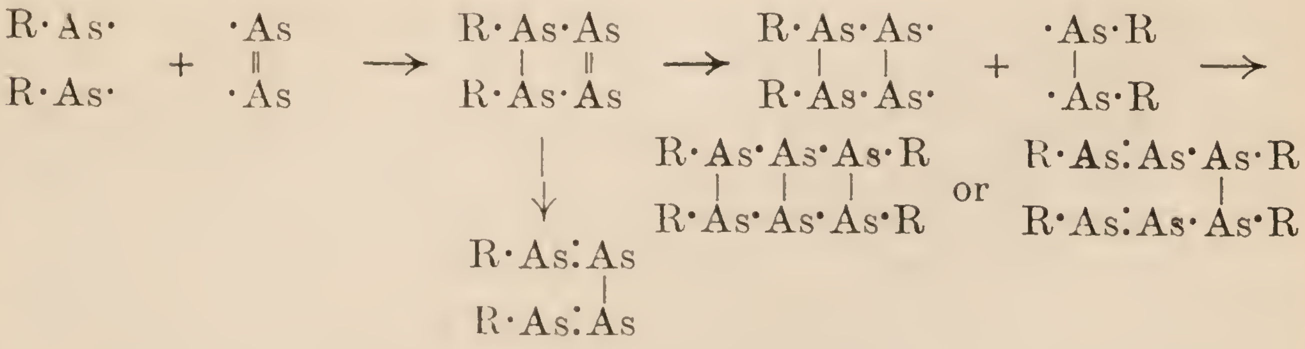
Of the polyarsenides described in the present communication, one—that obtained by the reduction of 5-nitro-4-hydroxy-3-methoxyphenylarsinic acid—supports the general formula R_2As_4, whilst another—that from 5-amino-3:4-dimethoxyphenylarsinic acid—agrees with a second type, R_2As_3 or R_4As_6. Of those prepared by Farbwerke vorm. Meister, Lucius & Brüning, one falls into each category.

The assumption of simultaneous reduction would require fission of the arsinic acid to precede reduction. The visual evidence suggests that, in the present instance, the reverse is the case, so the alternative mechanism has been assumed. It is supported by the observation that if a suspension of 3:3′-diamino-4:4′-dihydroxyarsenobenzene in the hyposulphite reduction mixture is treated with two molecular proportions of sodium arsenite and a further quantity of hyposulphite, the transition of the colour through reddish-brown finally to dull brown gradually takes place.

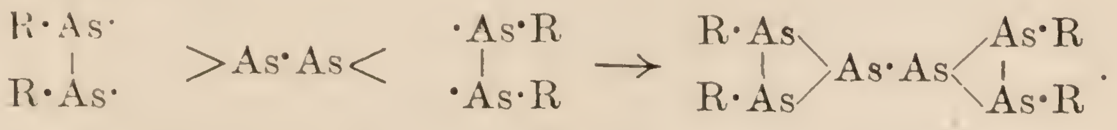
The reaction between two symmetrical arsenobenzenes to produce the unsymmetrical product may be represented as follows:



Its extension to the polyarsenical compounds permits of the formulation of the types R_2As_4 and R_4As_6 by the following stages:



or, alternatively,



The examination of the polyarsenides has, however, so far been too cursory to allow of any final statement as to their constitution, and it should be emphasised that the homogeneity of the products, assumed on purely chemical grounds, would be difficult to determine satisfactorily in compounds relatively so unstable and insoluble.

EXPERIMENTAL.

p-*Methoxyphenylarsinic Acid.*

This was prepared by the methylation of *p*-hydroxyphenylarsinic acid (*Ber.*, 1914, **47**, 276). The melting point has been variously given by Michaelis (*Ber.*, 1887, **20**, 2051; *Annalen*, 1902, **320**, 299) as 159—160° and 203°, and by Bertheim as 179—180°. The acid crystallised from water in long, prismatic needles, which melted at 182° (corr.), and formed the anhydride at a temperature of 130°, the loss indicating the presence of a quarter of a molecule of water of crystallisation, only removed at the temperature of anhydride-formation (Found: loss at 130° = 9·6, 9·5. $C_7H_9O_4As,\frac{1}{4}H_2O$, for loss of $1\frac{1}{4}H_2O$, requires 9·5 per cent. In product: C = 39·4; H = 3·4. $C_7H_7O_3As$ requires C = 39·3; H = 3·3 per cent.).

As it was thought that this might account for the differences in melting point recorded above, the acid was boiled for an hour with acetic acid containing a little acetic anhydride, and then set aside, when fan-shaped clusters of needles separated. The melting point, however, remained unaltered, although conversion into the anhydride showed the product to be anhydrous (Loss at 130° = 8·1. $C_7H_9O_4As$ requires for loss of $1H_2O$ 7·8 per cent.).

3-*Nitro*-4-*methoxyphenylarsinic Acid.*

To 4·6 grams of *p*-methoxyphenylarsinic acid dissolved in 15 c.c. of sulphuric acid and cooled to −10°, a mixture of 1·4 c.c. of nitric acid (D 1·4) and 1·4 c.c. of sulphuric acid was added, the temperature being kept at about −8°. The mixture, after remaining for twenty-four hours in a cool place, was poured on 100 grams of powdered ice, when an almost colourless, flocculent precipitate deposited, the yield amounting to 95 per cent. of the theoretical.

3-*Nitro*-4-*methoxyphenylarsinic acid* is sparingly soluble in cold water, but readily so in hot, from which it separates in minute needles, which begin to decompose above 290° (Found: C = 30·0; H = 3·1; N = 5·0; OMe = 10·9. $C_7H_8O_6NAs$ requires C = 30·3; H = 2·9; N = 5·05; OMe = 11·2 per cent.). The acid was identical with that obtained by the methylation of 3-nitro-4-hydroxyphenylarsinic acid. The product from this reaction, however, contained much unchanged starting material. Separation was effected by fractional crystallisation, the methylated acid being slightly the less soluble in water.

The *monosodium* salt crystallises in pale yellow needles containing $2H_2O$ (found: loss at 110° = 10·4. $C_7H_7O_6NAsNa,2H_2O$ requires $H_2O = 10·7$. In dried substance: Na = 8·0. $C_7H_7O_6NAsNa$ requires Na = 7·7 per cent.).

3-*Amino-4-methoxyphenylarsinic Acid.*

Five grams of 3-nitro-4-methoxyphenylarsinic acid were reduced in boiling methyl alcohol by 120 grams of 5 per cent. sodium amalgam. The solvent was removed by distillation, the residue dissolved in water, the solution decanted from mercury, and neutralised with hydrochloric acid. After concentration, the amino-acid gradually separated, and was purified by crystallisation from water, forming clusters of colourless needles, which melted and decomposed at 193° (corr.) (Found: N = 5·6; OMe = 12·7. $C_7H_{10}O_4NAs$ requires N = 5·7; OMe = 12·6 per cent.).

Many attempts were made to displace the amino-group by hydroxyl without success. When the diazotised solution was heated, no evolution of nitrogen took place, whilst experiments in which the temperature of the reaction was raised by the use of 10 per cent. sulphuric acid, a mixture of sodium sulphate and sulphuric acid, or a saturated solution of copper sulphate, led to almost complete decomposition. Similar results were obtained with 3-amino-4-hydroxyphenylarsinic acid. Experiments in which the acids were treated with sodium hydrogen sulphite were equally unsuccessful, and led to fission of the arsinic acid, the only isolable product being a small proportion of the unchanged acid.

4-*Aminoveratrole.*

The reduction of 4-nitroveratrole by tin and hydrochloric acid has already been described (*Bull. Soc. chim.*, 1896, [iii], **15**, 646; T., 1918, **113**, 28). The following method is, however, more satisfactory.

To a solution of 125 grams of crystalline sodium sulphide in a little water, 50 grams of 4-nitroveratrole (T., 1915, **107**, 257) were added, and the mixture was gently boiled for four hours, then cooled, and extracted with chloroform. The crude aminoveratrole was removed from the chloroform by dilute hydrochloric acid, and the combined extracts were basified, when most of the amine separated in a solid state and was collected, any base remaining in the filtrate being extracted by ether. The total yield amounted to 42 grams.

The acetyl derivative is very sparingly soluble in ether or light petroleum, more so in benzene, acetone, or ethyl acetate, and readily so in alcohol or hot water, from which it separates in glistening plates, which melt at 136° (corr.) (compare *Ber.*, 1896, **29**, 2690).

3:4-*Dimethoxyphenylarsinic Acid.*

A solution of 15 grams of aminoveratrole in 200 c.c. of 5 per cent. hydrochloric acid was diazotised with 7·1 grams of sodium nitrite, and added to 18 grams of arsenious oxide dissolved in 140 c.c. of 10 per cent. sodium hydroxide, nitrogen being immediately evolved. After several hours, the mixture was rendered strongly alkaline and warmed on the water-bath for half an hour, treated with charcoal, and acidified, when the acid gradually separated.

3:4-*Dimethoxyphenylarsinic acid* is very sparingly soluble in acetone, but readily so in alcohol or hot water, from which it separates in colourless, anhydrous, rhombic prisms. When placed in a bath at 170°, it melts at 192° (corr.), sintering from 187°. On slow heating, it sinters, but does not melt, between 180° and 190°. This behaviour is due to the readiness with which anhydride-formation takes place (Found: C = 36·4; H = 4·2; As = 28·6. $C_8H_{11}O_5As$ requires C = 36·6; H = 4·2; As = 28·6. Loss at 140° = 7·1. $C_8H_{11}O_5As$ requires for loss of $1H_2O$, 6·9 per cent.). The ammoniacal solution yields a voluminous precipitate of minute needles on boiling with calcium chloride, and an amorphous precipitate with magnesia mixture. With warm dilute hypophosphorous acid, a white, amorphous precipitate of 3:4:3′:4′-*tetramethoxyarsenobenzene* is obtained. When heated with hydrobromic acid at 100°, or with hydrochloric acid of varying concentrations at temperatures of 130° to 160° to effect partial demethylation, fission of the arsinic acid grouping takes place, only a small proportion of partly methylated acid being obtained.

5-*Nitro*-3:4-*dimethoxyphenylarsinic Acid.*

The preparation of this acid was carried out as described in the case of 3-nitro-4-methoxyphenylarsinic acid (p. 868), the yield amounting to 85 per cent. of the theoretical. It separates from boiling water in clusters of minute needles, which melt and decompose at 236° (corr.). Reduction with sodium hyposulphite leads to a reddish-brown solution, but no precipitate (Found: C = 31·1; H = 3·3; N = 4·6; As = 24·2. $C_8H_{10}O_7NAs$ requires C = 31·3; H = 3·3; N = 4·6; As = 24·4 per cent.).

The *monosodium* salt crystallises in glistening, flattened prisms, which lose their lustre when dried in the air and contain $6H_2O$ (Found: loss at 110° = 24·7. $C_8H_9O_7NAsNa,6H_2O$ requires $H_2O = 24{\cdot}7$. In dried material, Na = 6·9. $C_8H_9O_7NAsNa$ requires Na = 7·0 per cent.).

The *barium hydrogen* salt crystallises as a matted mass of faintly yellow needles, which contain $3H_2O$ (Found: loss at 110° = 6·7. $(C_8H_9O_7NAs)_2Ba,3H_2O$ requires $H_2O = 6{\cdot}7$. In dried material, Ba = 18·2. $(C_8H_9O_7NAs)_2Ba$ requires Ba = 18·3 per cent.).

Although the acid is more stable towards mineral acids than 3 : 4-dimethoxyphenylarsinic acid, its hydrolysis does not afford a suitable means of preparing the corresponding partly methylated and demethylated acids. At 160° with concentrated hydrochloric acid, it is largely decomposed, but at 130° slow hydrolysis of the methoxyl groups takes place, and crystallisation of the product yields from the more soluble fractions a proportion of a partly methylated acid, separating from water in slender prisms and melting and decomposing at about 254° (corr.). It is apparently identical with 5-*nitro*-3-*hydroxy*-4-*methoxyphenylarsinic acid* (p. 874) (Found: C = 28·9; H = 3·0; OMe = 11·0. $C_7H_8O_7NAs$ requires C = 28·7; H = 2·75; OMe = 10·6 per cent.).

5-*Amino*-3 : 4-*dimethoxyphenylarsinic Acid*.

The foregoing acid was reduced by ferrous hydroxide in alkaline solution (compare *J. Amer. Chem. Soc.*, 1918, **40**, 1581), the yield amounting to about 85 per cent. of the theoretical. 5-*Amino*-3 : 4-*dimethoxyphenylarsinic acid* dissolves sparingly in cold water or alcohol, but readily in dilute mineral acids or hot water, from which it separates in radiating clusters of needles melting and decomposing at 173° (corr.). The solution in dilute hydrochloric acid gives a bright red coloration with a trace of potassium dichromate, and, after treatment with nitrous acid, a deep red coloration with sodium-β-naphthoxide. The aqueous solution develops a reddish-brown colour with ferric chloride. The ammoniacal solution gives no precipitate on warming with magnesia mixture or with barium chloride, but with calcium chloride a heavy, crystalline precipitate (Found: N = 5·0; As = 27·3. $C_8H_{12}O_5NAs$ requires N = 5·05; As = 27·05 per cent.).

Reduction of 5-*Amino*-3 : 4-*dimethoxyphenylarsinic Acid*.

(*a*) *With Sodium Hyposulphite*.—The reduction was carried out as described in the case of 5-nitro-4-hydroxy-3-methoxyphenylarsinic acid (p. 873). The pale yellow precipitate deepened in colour as the reaction proceeded. It was collected, washed very thoroughly with water and with alcohol, and dried in a vacuum, first at the ordinary temperature, and finally at 60° for analysis. The ratio of arsenic to the other elements present indicated 3 atoms of arsenic to 2 benzene nuclei. It dissolves sparingly in the usual organic solvents, but readily in dilute acids (Found: C=37·3, 37·3; H=4·0, 3·9; N=5·2; As=41·4. $C_{16}H_{20}O_4N_2As_3$ requires C=36·3; H=3·8; N=5·3; As=42·5 per cent.).

(*b*) *With Hypophosphorous Acid.*—Reduction with dilute hypophosphorous acid at 60° yielded a black precipitate, which was isolated as in the previous instance (Found: As=93·0; C=2·6, 2·9; H=0·54, 0·60).

The composition of these products is discussed in the introduction.

4-*Hydroxy*-3-*methoxyphenylarsinic Acid.*

A suspension of 25·2 grams of 4-nitroguaiacol in 90 c.c. of concentrated hydrochloric acid was reduced by the gradual addition of 42 grams of tin. The resulting solution was freed from tin, diazotised with 12 grams of sodium nitrite, and added to an ice-cold solution of 27 grams of arsenious acid in 210 c.c. of 10 per cent. sodium hydroxide, the solution being maintained distinctly alkaline. As soon as the evolution of nitrogen ceased, the product was heated for half an hour on the water-bath, acidified to methyl-orange by means of hydrochloric acid, treated with charcoal to remove coloured impurities, evaporated to dryness under diminished pressure, and extracted with alcohol. The extract, amounting to about 25 grams, was dissolved in boiling water, when, after separation of a small quantity of a very sparingly soluble substance (*A*), 12·5 grams of 4-*hydroxy*-3-*methoxyphenylarsinic acid* were obtained. The acid is sparingly soluble in cold water or alcohol, but readily so in acetic acid or in hot water, from which it separates in stout, glistening, rhombic prisms containing $1H_2O$. After drying at 110°, it melts at 190° (corr.) (Found: loss at 110°=7·1. $C_7H_9O_5As,H_2O$ requires 6·8. In dried material, C=34·2; H=3·8; As=30·3. $C_7H_9O_5As$ requires C=33·9; H=3·7; As=30·2 per cent.). The ammoniacal solution gives no precipitate on boiling with barium chloride or magnesia mixture, but yields a crystalline precipitate of the *calcium* salt with calcium chloride. On warming the acid with a dilute solution of hypophosphorous acid, a colourless precipitate of 4:4′-*dihydroxy*-3:3′-*dimethoxyarsenobenzene* is obtained.

The *acetyl* derivative crystallises from ethyl acetate containing a little alcohol in colourless, glistening plates, which melt at 186° (corr.), sintering from 182°. It is readily soluble in water or alcohol, but sparingly so in ether or ethyl acetate (Found: C=37·5; H=4·1. $C_9H_{11}O_6As$ requires C=37·25; H=3·8 per cent.).

The sparingly soluble material (*A*), which was isolated only in minute quantity, proved to be 4:4′-*dihydroxy*-3:3′-*dimethoxydiphenylarsinic acid*. It separated from much water in radiating clusters of minute prisms containing $1\frac{1}{2}H_2O$, and melted at 234° (corr.), sintering from 227°. The ammoniacal solution of the acid gave a precipitate on warming with barium chloride, but not with magnesia mixture (Found: loss at 110°=6·7. $C_{14}H_{15}O_6As,1\frac{1}{2}H_2O$ requires 7·0. In dried material, C=47·3; H=4·4; As=21·2. $C_{14}H_{15}O_6As$ requires C=47·5; H=4·3; As=21·2 per cent.).

5-*Nitro*-4-*hydroxy*-3-*methoxyphenylarsinic Acid.*

The nitration of 4-hydroxy-3-methoxyphenylarsinic acid was carried out as already described (compare p. 868). Separation did not take place until the bulk of the mineral acid was neutralised by the addition of anhydrous sodium carbonate, when 3·2 grams of the nitro-acid were obtained. On crystallisation from boiling water, it formed glistening leaflets, which decomposed gradually above 260° without melting (Found: As = 25·5; N = 4·8. $C_7H_8O_7NAs$ requires As=25·6; N=4·8 per cent.).

On warming with a dilute solution of hypophosphorous acid, a bright yellow, granular precipitate of 5:5′-*dinitro*-4:4′-*dihydroxy*-3:3′-*dimethoxyarsenobenzene* was obtained.

5:5′-*Diamino*-4:4′-*dihydroxy*-3:3′-*dimethoxyarsenobenzene.*

To a solution of 3·5 grams of the above acid in 60 c.c. of water and 12 c.c. of 2*N*-sodium hydroxide was added a solution of 30 grams of sodium hyposulphite and 10 grams of magnesium chloride in 170 c.c. of water. The mixture was heated in an atmosphere of carbon dioxide at 60° for one and a-half hours, the arsenobenzene then collected, washed with water, dissolved in methyl alcohol containing hydrogen chloride, and the hydrochloride precipitated by the addition of dry ether. The product amounted to 2·1 grams of a faintly yellow powder, readily soluble in water and methyl alcohol, less so in ethyl alcohol, and insoluble in ether or acetone. The aqueous solution reacts faintly acid to methyl-orange. When dried to constant weight in a vacuum over sulphuric acid, it retains solvent equivalent to two molecules of water. It decomposes sharply at 186° (corr.). The addition of dilute sulphuric acid to the aqueous solution does not cause precipitation of the sulphate, but concentrated hydrochloric acid causes precipitation of the *hydrochloride* (Found: As=27·9; N=5·1;

Cl = 12·7. $C_{14}H_{16}O_4N_2As_2,2HCl,2H_2O$ requires As = 28·0; N = 5·2; Cl = 13·2 per cent.). This substance was submitted to biological test by Dr. R. A. O'Brien, of the Wellcome Physiological Research Laboratories, the results indicating that it was only slightly more toxic than salvarsan.

3-*Hydroxy*-4-*methoxyphenylarsinic Acid.*

This acid was prepared from 5-nitroguaiacol in the same manner as 4-hydroxy-3-methoxyphenylarsinic acid (p. 872) was obtained from 4-nitroguaiacol. From 21 grams of the nitroguaiacol, 8 grams of the pure acid were obtained. 3-*Hydroxy*-4-*methoxyphenylarsinic acid* separates from water in short, stout, flattened prisms containing one molecule of the solvent, which is lost at 110°. It then melts at 189° (corr.). The pure acid dissolves sparingly in alcohol or the other usual organic solvents (Found: loss at 110° = 7·3. $C_7H_9O_5As,H_2O$ requires 6·8. In dried material, C = 34·2; H = 3·8; As = 30·1. $C_7H_9O_5As$ requires C = 33·9; H = 3·7; As = 30·2 per cent.). The ammoniacal solution gives no precipitate on boiling with barium chloride or magnesia mixture, but yields a precipitate with calcium chloride. On warming with a dilute solution of hypophosphorous acid, the acid yields a colourless precipitate of 3 : 3′-*dihydroxy*-4 : 4′-*dimethoxyarsenobenzene.*

The *acetyl* derivative crystallises from benzene containing a little alcohol in woolly needles, which decompose gradually above 200°. It is readily soluble in water, alcohol, or ethyl acetate, but very sparingly so in benzene or light petroleum (Found: C = 37·5; H = 4·0. $C_9H_{11}O_6As$ requires C = 37·25; H = 3·8 per cent.)

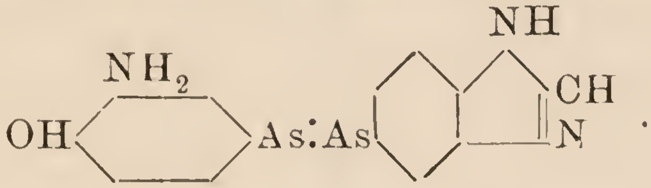
5-*Nitro*-3-*hydroxy*-4-*methoxyphenylarsinic Acid.*

The preparation of this acid was carried out in a similar manner to that of 5-nitro-4-hydroxy-3-methoxyphenylarsinic acid (p. 873); the yield amounted to 80 per cent. of the theoretical. The acid crystallises from water, in which it is somewhat sparingly soluble, in stellate clusters of prismatic needles, which melt at 252° (corr.), darkening gradually above 220° (Found: As = 25·6; N = 5·0. $C_7H_8O_7NAs$ requires As = 25·6; N = 4·8 per cent.). On reduction with warm hypophosphorous acid, it yields a bright yellow precipitate of 5 : 5′-*dinitro*-3 : 3′-*dihydroxy*-4 : 4′-*dimethoxyarsenobenzene.*

Reduction of 5-*Nitro*-3-*hydroxy*-4-*methoxyphenylarsinic Acid.*

The reduction was carried out, using sodium hyposulphite, as already described. The pale yellow precipitate first formed gradually darkened to brick-red as the reaction proceeded. It was collected, washed thoroughly with water, and dissolved in methyl alcohol containing hydrogen chloride, forming a blood-red solution, which deposited a reddish-brown precipitate of the *hydrochloride* on addition of ether. Analysis indicated that the product contained 2 atoms of arsenic to each benzene nucleus (Found: C=25·9; H=3·3; N=4·1; Cl=10·5; As=45·6. $C_{14}H_{16}O_4N_2As_4,2HCl$ requires C=25·9; H=2·8; N=4·3; Cl=10·9; As=46·2 per cent.).

3′-*Amino*-4′-*hydroxy*-1:3-*diazole*-5:1′-*arsenobenzene*,



A mixture of molecular proportions of 3-amino-4-hydroxyphenylarsinic acid and 1:3-benzodiazole-5-arsinic acid was reduced with sodium hyposulphite in the manner previously described. The product was converted into the hydrochloride by solution in methyl alcohol containing hydrogen chloride, and precipitation by ether. The yield amounted to about 85 per cent. of the theoretical.

The *hydrochloride* forms a pale yellow powder, readily soluble in water or methyl alcohol, less so in ethyl alcohol, and almost insoluble in ether or acetone. After drying for several hours in a vacuum over sulphuric acid, it retains solvent approximating to 3 molecules of water of crystallisation, of which one is lost at 60° and a second at 100° in a vacuum. On heating, it decomposes at 206° (corr.) (Found: C=32·1; H=3·8; N=8·3; As=30·4; Cl=14·0. $C_{13}H_{11}ON_3As_2,2HCl,3H_2O$ requires C=31·1; H=3·8; N=8·4; As=29·9; Cl=14·1 per cent. Loss at 60° in a vacuum=3·7. Loss of $1H_2O$ requires 3·6. Loss at 100° in a vacuum=7·3. Loss of $2H_2O$ requires 7·2 per cent.).

The *base* dissolves readily and completely in sodium hydroxide or in methyl alcohol containing hydrogen chloride, thus differing distinctly from 5:5′-arseno-1:3:1′:3′-benzodiazole (T., 1919, **115**, 1372), which dissolves but sparingly in the former and is quite insoluble in the latter.

In conclusion, the author would thank Mr. F. P. Walton for assistance in the analysis of a number of the compounds described in the investigation.

WELLCOME CHEMICAL RESEARCH LABORATORIES,
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